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Simulation of Interfacial Fracture in Highly Crosslinked Adhesives

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ABSTRACT

The fracture of highly-crosslinked networks is investigated by molecular dynamics simulations. The network is modeled as a bead-spring polymer network between two solid surfaces. The network is dynamically formed by crosslinking an equilibrated liquid mixture. Tensile pull fracture is simulated as a function of the number of interfacial bonds. The sequence of molecular structural deformations that lead to failure are determined, and the connectivity is found to strongly control the stress-strain response and failure modes. The failure strain is related to the minimal paths in the network that connect the two solid surfaces. The failure stress is a fraction of the ideal stress required to fracture all the interfacial bonds, and is linearly proportional to the number of interfacial bonds. By allowing only a single bond between a crosslinker and the surface, interfacial failure always occurs. Allowing up to half of the crosslinker's bonds to occur with the surface, cohesive failure can occur.

INTRODUCTION

Adhesives present a complex problem for polymer theory. Progress has primarily occurred for adhesives with weak interfacial (i.e. van der Waals) strength [1] such as pressure sensitive adhesives [2] and polymer-polymer interfaces [3]. For strong adhesives with surface chemical bonds equivalent development is lacking. The difficulty of performing measurements on interfaces is a major obstacle in understanding adhesion problems. Recent experiments at Sandia have begun to study failure for the strong interface formed between an epoxy and a silicon wafer [4]. The interfacial structure is probed with neutron and X-ray reflectivity. In addition, the number of chemical bonds at the interface is varied in a controlled manner through the use of self-assembled monolayer (SAM) coatings. In conjunction with these experiments, a program of molecular dynamics (MD) simulations has been developed [5]. Some initial results of these MD simulations are reported here.

SIMULATION DETAILS

Coarse-grained models have been very successful in describing polymer structure and dynamics [6]. A modification of the successful Kremer-Grest bead-spring model is used here [7]. Polymer chains are composed of beads which interact via a Lennard-Jones (LJ) interaction with a cutoff at $2.5d$.

DISCLAIMER

$$u_{LJ}(r) = 4u_0\left(\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6}\right) \tag{1}$$

where here u_0 is the LJ energy unit and d is the length unit and particle diameter. Beads are bonded together with a potential composed of two parts. The first part is just the purely repulsive version of the above LJ potential with a cutoff at $2^{1/6}$ d. A breakable bond potential was from a quartic potential

$$u_4(r) = \begin{cases} k_4(r-r_1)(r-r_2)^3 + U_0 & \text{for } r < r_2 \\ U_0 & \text{for } r \geq r_2 \end{cases} \tag{2}$$

The parameter set used is: $k_4 = 1434.3\ u_0/d^4$, $r_1 = 0.7411d$, $r_2 = 0.0$ and $U_0 = 67.2234\ u_0$.

The complete system consists of a polymer network between two walls (*cf.* Fig. 2). Each wall is composed of particles in two layers of an fcc lattice with nearest neighbor distance 1.204*d*. Here a 64x24 lattice is used.The (111) direction (*z*-direction) is perpendicular to the walls. The wall particles are bound to the fcc lattice sites by a harmonic spring with spring constant 100 u_0/d^2. The wall dimensions give the simulation cell lateral lengths, L_x and L_y. Periodic boundary conditions are used in these directions.The separation distance between the innermost wall layers is L_z. In the system discussed in this article the wall separation at the beginning of tensile pull is 39 *d*. The wall particles interact with the beads via the LJ potential in Eq. (1), and some wall particles are bonded to the polymer network by Eq. (2). The system contains 91,000 total particles. The dynamics of the system is performed at constant temperature using the Langevin thermostat. The integration time step is 0.005 τ, and the damping constants are 1 τ^{-1} for the monomers and 5 τ^{-1} for the walls.

The focus is on adhesives such as epoxies which have short strands. Epoxies are chemically cured networks formed from a liquid mixture of a resin (e.g. diglycidyl ether of bisphenol A) and a crosslinker (e.g. T403). They form highly crosslinked molecular networks with each strand consists of only a few monomers. Each bead corresponds typically to 2 or 3 monomers [7]. A bead-spring model with two beads per strand was found to be the best match to epoxy material property data.

To create a random network similar to epoxy networks, a liquid mixture is crosslinked dynamically. The mixture consists of two bead and three bead molecules. The three bead molecule has a sixfold functional crosslinker bead already bonded to a two bead strand. The strand beads and crosslinker beads have identical potential parameters. Bonds are formed when the separation between a crosslinker and a strand end or wall particle is less than 1.3 *d*. After equilibrating the liquid mixture, crosslinkers are first bonded to the walls. Next, during a MD run typically of 150,000 time steps, the crosslinkers are bonded to strands until at least 95% of all possible bonds are made. Zero load is maintained on the walls during the crosslinking. Afterward, the temperature is reduced below the glass transition temperature (0.5 u_0) to 0.3 u_0. This takes from 50,000 to 150,000 times steps with more steps required for the larger systems. The tensile pull is performed by moving the top and bottom walls apart at constant velocity. The tensile or normal stress is calculated from the total force on the wall divided by the wall area.

To study the fracture behavior as a function of the number of bonds across the interface, a grid pattern is used to restrict bonds to occur only in a designated area. The wall surface is covered by a grid; 8x3 was used. Within each grid a central rectangle determines the region where bonds to surface are not allowed. By varying the size of this region, the bonding to the walls can be varied from 0% to 100%.

RESULTS

Figure 1(a) shows tensile stress-strain curves as a function of areal bond coverage, *C*. For full bonding ($C = 1$) the correspondence between the molecular deformations and the stress-strain curve is as follows. The first peak at $\varepsilon_y = 0.1$ is the yield stress. There is a maximum in the LJ force to separate neighboring pairs of beads. In equilibrium, the typical separation is 1 *d*, and the maximum force is at $r = 2^{1/6}\,d = 1.12\,d$. Thus it takes a strain of about 0.1 to reach the maximum value. For $\varepsilon > \varepsilon_y$ the stress remains constant for a wide range of strains. In this plateau regime, examination of configurations shows that the bonds are not stretched. Instead the strands (including the crosslinkers) connecting two crosslinkers are pulled progressively taut. Only after the strands are in the taut, linear conformation do the bonds begin to stretch. At this point, the stress rises. The points show the strains at which bonds break. The first bond breaking occurs at $\varepsilon = 0.78$. As more bonds are stretched the stress rises and additional bonds break. Finally, the system fails at $\varepsilon_f = 1.02$, where the failure strain is taken as the strain at the midpoint between the failure stress (peak) and zero stress. Failure is interfacial with all the bonds between the bottom surface and the network breaking.

To understand the failure strains in terms of the network structure, we need to know what is the maximum strain possible without bonds breaking. An upper limit to the strain at which

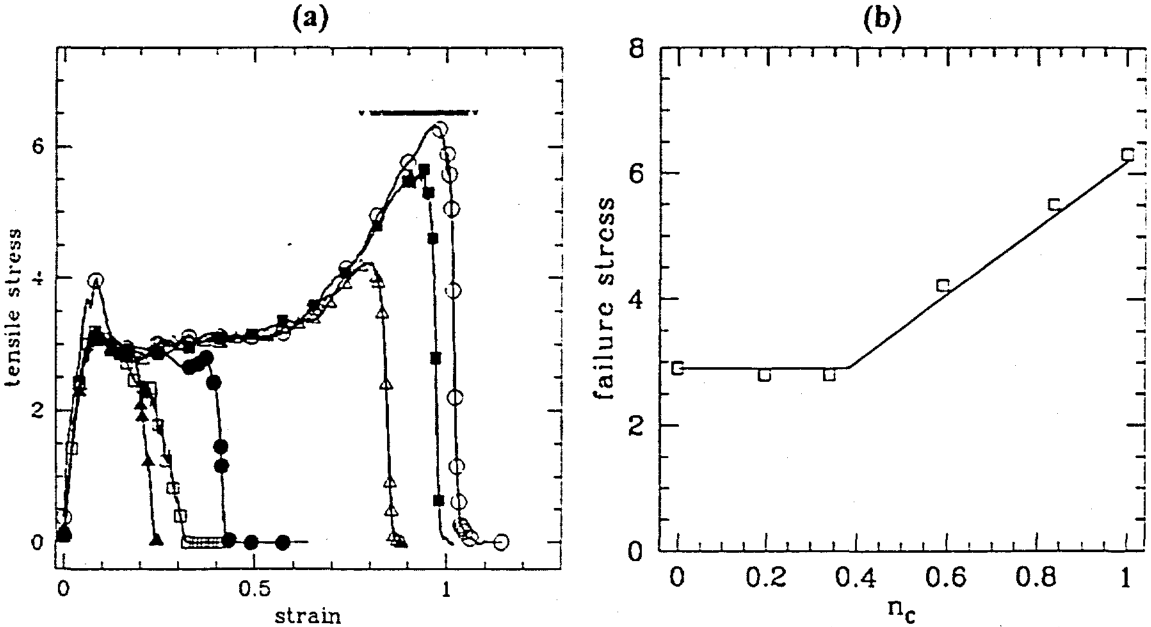

Figure 1. (a) The tensile stress-strain curves for different bondable area fraction C at the bottom surface: 0% (▲), 10% (□), 25% (●), 50%, (Δ), 75% (■), 100% (O). The crosses indicate the strains at which bond breaking occurs for the C=100% case. (b) The failure stress as a function of the fraction of interfacial bonds n_C shows a flat regime dominated by van der Waals and linear regime of purely interfacial bond fracture.

scission must occur is given by the minimal path lengths of the network. For a site on the bottom wall to which the network is bonded, there are many paths through the polymer network to the top wall. The shortest path is the minimal path P for that site on the bottom wall. For the complete system there is a set of minimal paths, one for each bonding site at the bottom wall. The strain at which the strands in a minimal path are taut, but the bonds are not stretched is given by the relation, $\varepsilon_P = (P - L_z) / L_z$, where L_z is the unstrained separation distance between the walls. For $\varepsilon > \varepsilon_P$, some bond within the minimal path must stretch. Using Dijkstra's method [8], P has been calculated for all bonding sites on the bottom wall. For the $C = 1$ system in Fig. 1(a) the shortest minimal path has $\varepsilon_P = 0.73$ which is slightly smaller than the first broken bond indicated by the points in the figure. Additional strain is required to stretch bonds to the breaking point. The simulations show that $(P_{ave} - L_z) / L_z$ is a good estimate of the failure strain, where P_{ave} the average minimal path over the whole system. For the $C = 1$ system in Fig. 1 the average value corresponds to $\varepsilon_P = 0.92$ which is about where the peak (failure) stress occurs.

The number of bonds across the interface is an important quantity affecting interfacial fracture. The ideal stress to fracture the interfacial bonds is directly proportional to the number of interfacial bonds, N_b, $\sigma_{id} = N_b F_b / A$, where F_b is the force to break a single bond and A is the area of the interface. For systems in Fig. 1, $\sigma_{id} = 16.3\ u_0/d^3$. This ideal value never occurs in the simulations, because the bonds are broken sequentially, not simultaneously (Fig. 1). Thus, at any given instant the contribution to the total stress by bond breakage is a fraction of the ideal value. The failure stress in Fig. 1 is $\sigma_f = 6.2\ u_0/d^3 = \sigma_{id} / 2.6$.

While σ_f at $C = 1$ is not equal to σ_{id}, the scaling as a function of C is the same. Let $n_C = N_b(C) / N_b(C{=}1)$. Then, the fracture stress at C is $\sigma_f(C) = N_b(C)\, F_b / A + \sigma_{vdW} = n_C\, \sigma_f(C{=}1) + \sigma_{vdW}$, where σ_{vdW} is the van der Waals (LJ) contribution to the fracture stress. Figure 1(b) shows that for $n_C > 0.4$, this linear relation is satisfied. For $n_C < 0.4$, the number of interfacial bonds is sufficiently small that surface van der Waal interactions dominate the fracture process. Thus, the failure stress is constant.

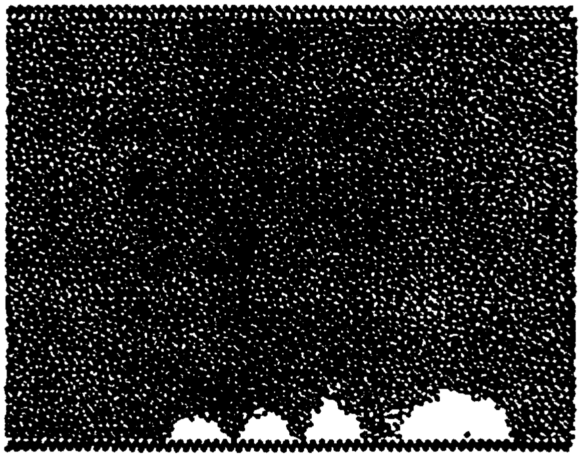

Figure 2. Image of the C=10% system at ε = 0.25. The surface voids are clearly visible.

The failure strain at $C = 1$ is determined by the minimal paths in the network. For $C < 1$, the failure strains are smaller (see Figure 1(a)). For this to happen, bonds must stretch before the minimal paths become taut. An inhomogeneity in the strain profile can cause path segments to become taut before the whole segment. Since the walls are pulled at constant velocity, a homogeneous strain would yield a linear displacement profile. For $C < 1$, significant devations from the linear profile occur at the interface. The mechanism for these deviations is exhibited in Fig. 2. The figure shows an image of a tensile pull simulation at $C = 0.1$ and $\varepsilon = 0.54$. Nanometer scale cavities have formed on the bottom surface above the regions which are not chemically bonded to the bottom surface. The initial pull off occurs at about the same strain as for the completely nonbonded system. The consequence of the interfacial cavities is that the displacement of monomers near the bottom surface from their initial position is larger than the uniform linear profile. Thus, the bonds to the surface are more strained the fewer the interfacial bonds and the larger the pull off regions. In the $C = 0.1$ system at $\varepsilon = 0.54$, the stress has already dropped to 1.0 u_0/d^3 from the plateau stress (see Fig. 1(a)). Most of the drop in the stress is due to this pull off as it occurs before the bonds break.

All the simulations discussed above fractured interfacially, as crosslinkers were allowed to only form at most one bond to the surface. For the crosslinker bonded to the surface, the single bond to the surface must support on average three times the force that each (of the three) bond between the crosslinker and the network must support. Thus, the surface bond stretches more and breaks resulting in interfacial failure. If multiple (up to three) bonds between a crosslinker and the surface is allowed, then preference for interfacial failure should decrease. Such simulations have been performed. Calculation of the bond density in layers perpendicular to the surface show that the number of bonds at the surface has a minimum at several d away from the surface. Figure 3 shows that cohesive failure occurs in this system. Thus, interfacial bond density determines the nature of the failure, adhesive vs. cohesive.

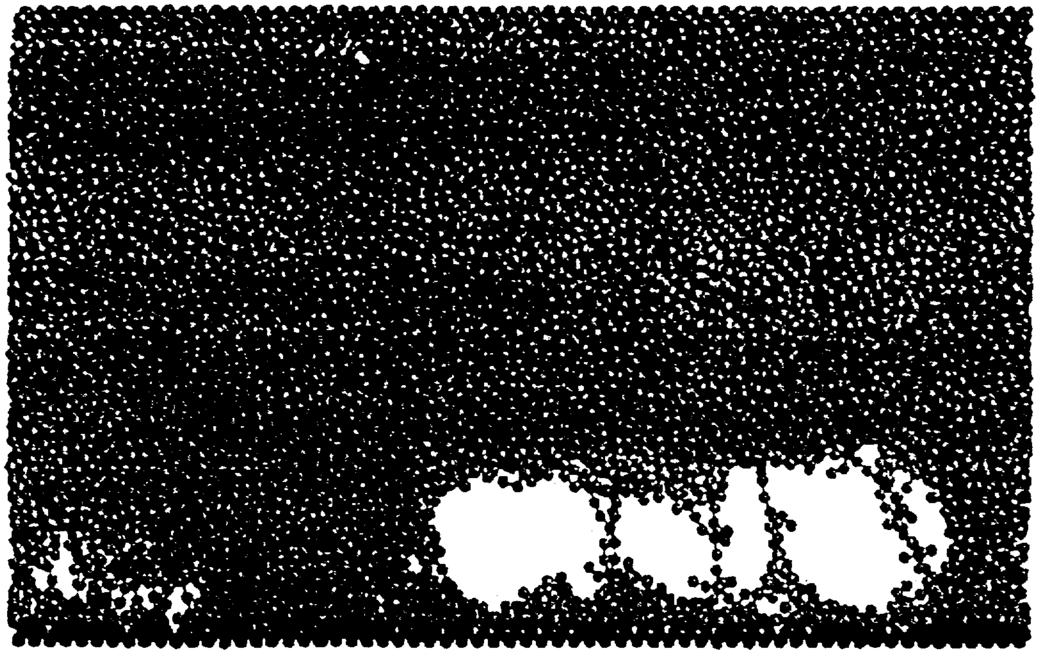

Figure 3. Image of a C=1 (51000 particle) system with multiple surface bonds per crosslinker. An intermediate stage of the cohesive fracture is shown.

CONCLUSION

Initial molecular dynamics simulation results have been presented for fracture of highly crosslinked polymer networks bonded to a solid surface. The correspondence between the stress-strain curve and the sequence of molecular deformations has been detailed. For the present model, bonds are not stretched until strains much larger than the yield strain have been reached. The failure strain for a fully bonded surface is equal to the strain necessary to make taut the average minimal path through the network from the bottom solid surface to the top surface. At bond coverages less than full, cavities form at the surface over the nonbonded regions. This yields an inhomogeneous strain profile with a bulk and an interfacial term. This inhomogeneous strain is an additional constraint on the network which results in segments of the minimal path near the interface becoming taut well before the full path. The failure stress has a linear dependence on the number of interfacial bonds. The simulations show that sequential bond breaking reduces the fracture stress below the ideal value. The number of interfacial bonds determines whether the failure mode is adhesive or cohesive.

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